

The Chemistry of Fluorescent Lamps and the Chemistry of Getting Rid of Them

Brief History

- **1857 - Henri Becquerel - French chemist explores fluorescence and speculates about practical use**
- **1901 - Peter Cooper Hewitt (American) patents the first mercury vapor lamp**
- **1936 - George Inman & Richard Thayer, at General Electric, patent fluorescent lamp**
- **1938 - First commercial GE lamps sold**

How they work

- Mercury vapor in the lamp is easily ionised, allowing current flow throughout the tube and raising electrons to a higher shell
- When the electrons drop back down UV light is emitted - Blacklight
- UV excites the phosphors, and when those electrons drop down they emit visible light

GE Phosphor Constituents

- Halophosphate- calcium chloro-fluoro-phosphate, with small amounts (< 1-2% by weight) of antimony and manganese
- Mixture of rare earth elements-lanthanum, yttrium as either an oxide or as a phosphate, along with a barium/aluminum oxide.

Philips Constituents

SECTION 2: HAZARDOUS INGREDIENTS

LAMP ASSEMBLY

	<u>% by Wt.</u>
Inert Ingredients (Glass, Al, etc.)	Approx 98%
Phosphor Powder	Approx 2%
Fluorides* (as F)	Approx 0.01%
Antimony*(7440-36-0)	Approx 0.01%
Manganese*(7439-96-5)	Approx 0.02%
Aluminum Oxide (1344-28-1)	Approx 0.01%
Mercury(7439-97-6)	< 20 ppm

*These materials are tightly bound within the crystal matrix of the phosphor (Calcium Phosphate).

Sylvania Constituents

Chemical Name	CAS #	% by Wt
Glass (soda lime)	_____	75 - 95
Mercury	7439-97-6	0.002 - 0.02
Lead Oxide	1317-36-8	0.2 - 2.0
Aluminum Oxide		
Fluorescent Phosphor & cathodes may contain		0.5 - 3.0
Fluoride (as F)	_____	0 - 0.1
Manganese (as dust)	7439-96-5	0 - 0.1
Tin (as dust)	7440-31-5	0 - 0.1
Yttrium (as dust)	7440-65-5	0 - 0.5
Barium (as dust)	7440-39-3	< 0.1
Tungsten (as dust)	7440-33-7	< 0.1
Strontium (as dust)	7440-24-6	0 - 0.1
Magnesium (as dust)	7439-95-4	0 - 0.1
Calcium (as dust)	_____	0 - 0.1
Antimony (as dust)	7440-36-0	0 - 0.1
Zinc (as dust)	7440-66-6	0 - 0.1
Europium (as dust)	7440-53-1	0 - 0.1
Cerium (as dust)	7440-45-1	0 - 0.1
Lanthanum (as dust)	7439-91-0	0 - 0.1
Terbium (as dust)	7440-27-9	0 - 0.1
Aluminum (as dust)	7429-90-5	0 - 0.1

Mercury in Fluorescent Lamps

- **Metallic - Est 0.02 mg in T8 lamp**
- **Divalent - various salts - 9.98 mg in phosphor in T8 lamp**

How they fail

- As a fluorescent tube is used, elemental mercury in the tube reacts with the phosphor coating, glass, electrode materials and lead wires. The elemental mercury also converts over time to soluble mercury compounds. Source: Sylvania

Mercury in the Environment - Big Picture

- **1995 -total global annual input of 5,500 tons Hg to the atmosphere from all sources - U.S. anthropogenic emissions contributed about 3 percent, or 158 tons. Fossil fuel powered electric generation = 84 tons (53 % of US total)**
- **Studies suggest that the total atmospheric mercury burden has increased by a factor of between 2 and 5 since the beginning of the industrial age.**
- **98% of Hg deposition in surface water comes from atmospheric deposition**

Why they are so wonderful

- 3 to 4 times more efficient than incandescent
- Incandescent lamps output around 10 to 20 lm/W, fluorescent tubes, up to 70 lm/W.
- EPA est. power plant emissions rate of 0.016 mg Hg/kwh so -
- 100 watt/hr incandescent bulb x 20,000 hrs x Hg rate = est. 320 mg or air emitted Hg per life of bulb
- 30 watt/hr fluorescent bulb x 20,000 hrs x Hg rate = 96 mg + 10 mg = 106 mg Hg

History of Lamp Designation

- '92 - EPA/NEMA initiated SAIC study-
developed test protocol, said lamps were HW
- '94 - EPA Proposed rule - UW or Exemption ?
- '95 - Philips announces Green Tip lamp
- '98 - EPA - Mercury Emissions from the Disposal of
Fluorescent Lamps- model to estimate Hg
emission
- '99 - EPA Final Rule - Universal Waste

1998 EPA Study

- **Estimated emissions from Conditional Exemption (CE) exemption or Universal Waste (UW) options**
- **For 2004, EPA estimated about 900 million lamps disposed**
- **The model estimates 2004 lamp disposal emissions at 740 kg for CE option and 685kg for UW option**

Total Mercury in Lamps

- < 1996 - about 30 mg / T8 lamp
- 1996 - 1999 - about 15 mg / T8 lamp
- 2000 - 2007 - about 10 mg / T8 lamp

Source:EPA

- 1985 - 48.2 mg / Avg 4' lamp
- 1999 - 11.6 mg / Avg 4' lamp Source: NEMA

Designation Procedure

- Toxicity Characteristics Leaching Procedure (TCLP) is designed to simulate conditions in a landfill
- Bulb is carefully smashed up
- Agitated in pH5 solution for 18 hrs
- Gas chromatography used to determine concentration of metals
- 0.2 mg/L (ppm) of Mercury = Hazardous Waste

TCLP

**0.2 mg/L Mercury = 7.05479 Ounces in
Olympic swimming pool**

**2 Packs of
Trail Mix
and a Pack
of Peanuts =
One Pool of
Hazardous
Waste**

Melbourne, 1956



How they Pass

- Philips- pellet that meters exact amount of Hg
- “Buffering” mechanism that prolongs the effectiveness of Hg, so less is required for long life
- “Iron Shield” that reacts during TCLP test to reduce leachable Hg Source: Sylvania website

How they Pass 2

- **GE -Ascorbic Acid in base cement is reactive**
- **Sylvania - copper-carbonate base cement or zinc plated iron lamp caps Source - Philips website**
- **Decreased leachability or test interference?**

Low Hg Bulbs Tested by WC

TCLP (ppm)

Bulb	Hg	Pb	Ba
	(limit 0.2 ppm)	(limit 5.0 ppm)	(limit 100.0 ppm)
1	0.12	0.11	1.0
2	0.05	0.10	< 1
3	0.07	0.80	< 1
4	0.09	< 0.1	< 1
5	0.09	< 0.1	1.1

The problem with Green Tips

- **Site Contamination**
- **Worker safety**
- **Fate in landfill -bacteriological
production of methylmercury**

How Much Mercury Does it Take?

In WA State,

1.28 oz of Hg (pack
of crackers)

in a 20 TON

DUMP TRUCK =

MTCA

Contaminated Site =

3628 broken tubes



Mercury and Health - Metallic

- Dental amalgam particles are our largest source
- Metallic vapors escape when fluorescent bulb is broken
- Lowest Observable Effects - Dentists showed motor skill, memory impairment, higher aggression levels - exposure measured at 0.014 mg/m³/day
- Hg vapor in broken lamp - .04 mg so- you'd have to break 8 bulbs to exceed dental exposure levels in same size room

Mercury and Health - Methylmercury

- **MeHg - $\text{CH}_3\text{Hg}^{++}$, CAS # 22967-92-6**
- **Highly toxic, crosses placental barrier & breast milk**
- **Causes permanent neurological damage, esp to developing fetuses**
- **Bioaccumulates - largest exposure risks are from fish**
- **EPA RfD = 0.1ug/kg/day - In WA white tuna Hg mean concentration = 214.5 ppb - one tunafish sandwich for a small individual. Some fish species up to 4.4 ppm**

Mercury and Health

Other sources -

Inorganic Hg - Non-fish foods

occupational

manufactured products -

**fluorescent. tubes, thermometers, switches,
chemistry, paint, fungicides, herbal remedies**

Down in the Dumps

- EPA estimates about 900 million lamps disposed in 2004 (at 12 mg/tube = 11.9 tons Hg)
- EPA 2004 est - 64% landfilled (7.6 tons) - studies detect little Hg in leachate or air emissions
- Fate in landfill - bacteriological production of methylmercury

Sources

**EPA - Mercury Emissions from the Disposal of
Fluorescent Lamps, 1998**

<http://www.epa.gov/epaoswer/hazwaste/id/merc-emi/merc-pgs/emmrpt.pdf>

NEMA - Fluorescent Lamps and the Environment

<http://www.nema.org/DocUploads/2BA10F1F-AA06-4C42-B1635A4148705054/nemafluorfinal.pdf>

**EPA - Binational Toxics Strategy- Mercury Sources and
Regulations, 1999 Update**

www.epa.gov/glnpo/bns/mercury/MercuryReport.pdf

Sources 2

**SAIC- Analytical Results of Mercury in
Fluorescent Lamps, 1992**

ATSDR Toxicological Profile - Mercury

**Toxicological Effects of Methylmercury -
2000**

<http://www.nap.edu/books/0309071402/html/>